TECHNICAL MEMORANDUM

August 26, 2003

To: Mr. Marc P. Smits

From: Todd H. Wiedemeier and W. Zachary Dickson

Subject: Recommendations for Well Installation Locations and Aquifer and Groundwater Analytical Data Required for Evaluating Monitored Natural Attenuation at Site 16, Operable Unit 3 at Marine Corps Air Station El Toro, California

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This technical memorandum was prepared by T.H. Wiedemeier & Associates, LLC (THWA) for the United States Navy (US Navy). The purpose of this memorandum is to provide guidance for the evaluation of monitored natural attenuation for chlorinated ethenes dissolved in groundwater at Site 16, Operable Unit 3 at Marine Corps Air Station El Toro, California. This memorandum is based upon a combination of the information provided in the United States Environmental Protection Agency (USEPA) *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater* (USEPA, 1998), Wiedemeier *et al.* (1999), Wiedemeier *et al.* (2002), THWA's experience evaluating monitored natural attenuation at hundreds of sites around the world, and our review of the following site-specific documents:

Bechtel National, Inc., *Comprehensive Long-Term Environmental Action Navy Clean II – Draft Final Phase II Remedial Investigation Report OU-3A Sites, Marine Corps Air Station El Toro, California, Volume III Attachments J-N, CTO-0079/0391,* dated June 1997.

Bechtel National, Inc., *Draft Phase II Feasibility Study, OU 3 Site 16, Crash Crew Training Pit No. 2,* dated February 2000.

Bechtel National, Inc., *Final Technical Memorandum Multiphase Extraction Pilot Study, Installation Restoration Program Site 16,* dated May 2002.

Bechtel Environmental, Inc., Final *Phase II Focused Feasibility Study Report, OU 3 Site 16, Crash Crew Training Pit No. 2,* dated August 2002.

Bechtel Environmental, Inc., *Draft Final Record of Decision for Operable Unit 3 Site 16, Crash Crew Training Pit No. 2,* dated May 19, 2003.

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Based upon our evaluation, THWA recommends the installation and sampling of eight (8) new monitoring wells and the sampling of seven (7) existing monitoring wells to evaluate the efficacy of monitored natural attenuation. THWA assumes that the installation of monitoring wells within the existing runway is allowable and will not cause hazard to planes that are taxiing, taking off from, or landing on the runway into which these wells will be installed. If any hazard could exist to any plane operating on this runway, then these wells should not be installed. If a potential problem exists then THWA will suggest alternate well installation locations. Figure 1 shows the locations of existing and proposed wells to be used for the evaluation of natural attenuation. With the exception of proposed well 16_MW14D which should be screened from 45 to 65 feet below the water table, all of the new wells should be screened from five (5) feet above the water table to 35 feet below the water table. For comparable results, the new wells should be constructed using the same techniques that were used for monitoring-well construction at Site 16 in the past. Table 1 lists the new and proposed monitoring wells to be sampled for this evaluation. Table 2 lists the aquifer data that should be collected from the existing and proposed wells. Total organic carbon, bulk density, and field observation and laboratory analysis of reduced iron minerals should be collected during the drilling of the boreholes for the proposed monitoring wells. Groundwater elevation data should be collected from all of the wells listed in Table 1 after the new monitoring wells have been installed and groundwater levels have stabilized across the site. These data will be used to calculate the groundwater flow direction and hydraulic gradient. Slug tests should be performed in at least five (5) wells to help estimate hydraulic conductivity for seepage velocity calculations. It is anticipated that estimates from literature values and a sensitivity analysis will be utilized to estimate porosity. Table 3 lists those groundwater analytical data required to evaluate monitored natural attenuation.

Sampling and analysis of groundwater in the new and existing monitoring wells, in conjunction with existing historical data, should allow an accurate analysis of monitored natural attenuation. In addition, if monitored natural attenuation is determined to be an appropriate remedial measure for Site 16, then the new and existing monitoring wells may be adequate for long-term monitoring of monitored natural attenuation.

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RATIONAL FOR PROPOSED FIELD AND LABORATORY CHEMICAL ANALYSES

The following presents the rational for the proposed field and laboratory analysis of the chemical conditions of the aquifer.

AQUIFER DATA

Aquifer data are useful for evaluating monitored natural attenuation. The following discussion describes the rational for the proposed aquifer analyses.

Field Observation of Iron Minerals

Qualitative information on the occurrence of reduced Fe(II) and iron sulfide minerals should be obtained by visual observation of samples collected during borehole drilling. Much of the color associated with sediments is provided by the presence of iron-based minerals and their oxidation state. In general there is a correlation between decreasing sediment size and increasing iron concentration (Kennedy *et al.*, 2000). For example, the presence of oxidized iron (Fe[III]) minerals can impart the following colors to sediments (Kennedy *et al.*, 2000):

Mineral	Color
Ferrihydrite ($FeOH_3$)	reddish brown
Göethite (FeO_2H)	yellow to orange
Hematite (Fe_2O_3)	red to maroon

Conversely, sediments containing reduced iron such as iron sulfide minerals are typically gray to black in color. Because FeS and FeS_2 cannot be differentiated visually in the field a simple field test to differentiate these materials is as follows (from Kennedy *et al.*, 2000):

Place a few grams of sediment into a small mouth bottle such as a 160 milliliter

serum bottle and add several milliliters of 6 N HCl. Cover the mouth of the bottle

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for 30 seconds. If FeS is present then the distinctive "rotten egg" odor associated with H_2S will be detected. Care should be taken to avoid inhaling too much of the gasses produced by this test. Because H_2S is a deadly gas, the person conducting the test should consult with their health and safety director to ensure that the site specific health and safety plan allows the use of this olfactory test.

In addition to these tests, a magnet can be used in the field to determine if minerals which can facilitate abiotic degradation such as magnetite are present.

Laboratory Mineralogical Analyses

There are many assays that can be done to determine the mineralogical composition of soil, sediment, and rock. It is best to contact a qualified laboratory for these analyses. In general the assay should include analyses for those reduced iron minerals which are known to facilitate abiotic degradation of chlorinated compounds (e.g., reduced iron minerals).

GROUNDWATER ANALYTICAL DATA

There are several groundwater analyses that can be used to evaluate and quantify natural attenuation. It is recommended that the analyses presented in Table 3 and discussed below be conducted for Site 16.

Daughter Products

Concentrations of chlorinated solvents and their degradation (daughter) products give a direct indication of the presence or absence of degradation (both abiotic and biological) processes. In many cases the production of *cis*-1,2-dichloroethene (*cis*-DCE), vinyl chloride

(VC), and chloride ions along aquifer flowpaths is direct evidence of intrinsic remediation. For example, if trichloroethene (TCE) was the only contaminant disposed of at a site, then any *cis*-1,2-DCE or VC present at the site must have come from the degradation of the parent TCE.

Non aqueous-phase liquid (NAPL) analyses can be helpful in establishing which compounds were disposed of at a site. At sites where it can be demonstrated that compounds appearing in groundwater were not disposed of these compounds are likely daughter products. It is possible that VC and some DCE isomers can be primary contaminants in some groundwater systems. However, VC is not normally present as a primary contaminant in solvent spills. The reasons for this are; 1) VC was not used as a solvent, and 2) VC is a gas at temperatures as low as 15°C. Thus, the presence of VC in groundwater associated with a chlorinated ethene spill is strong evidence of reductive dechlorination. Also, *cis*-DCE (rather than *trans*-DCE or 1,1-DCE) is usually produced from the reductive dechlorination of TCE (both abiotically and biologically). As a rule of thumb, if the ratio of *cis*-1,2-DCE to *trans*-1,2-DCE plus 1,1-DCE is greater than about 5:1, then the DCE is likely the result of degradation of TCE and/or PCE. When 1,1,1-TCA is present or is suspected to have been present, 1,1-DCE may be present as the result of the abiotic dehydrohalogenation of this compound. This must be taken into account when evaluating the ratio of DCE isomers. Based on these concepts, VC and/or *cis*-DCE are usually reliable indicators of reductive dechlorination. In addition, the presence of ethene and ethane typically are indicative of reductive dechlorination. However, these products are extremely transitory and low detection limits typically are required to identify and quantify these compounds.

Dissolved Oxygen

The concentration of dissolved oxygen in an aquifer is a very important parameter for determining if the system is capable of supporting the degradation of chlorinated solvents in the terrestrial subsurface. If dissolved oxygen is present at concentrations greater than about 0.5 mg/L (assuming accurate measurements) then reductive dechlorination (biological or abiotic) will not occur to any significant extent.

Dissolved oxygen is the favored electron acceptor used by microbes for the biodegradation of most forms of organic carbon. Strictly anaerobic bacteria generally cannot function at dissolved oxygen concentrations greater than about 0.5 mg/L and hence Fe(III) reduction, sulfate reduction, methanogenesis, and reductive dechlorination (biological or abiotic) cannot occur. Therefore, it is important to have a source of carbon in the aquifer that can be used by aerobic microorganisms as a primary substrate. During aerobic respiration, dissolved oxygen concentrations decrease. The absence of dissolved oxygen is a prerequisite for iron- and sulfate-reduction.

Dissolved oxygen measurements should be taken during well purging and immediately before sample acquisition using a direct-reading meter in a flow-through cell. Each of these measurements should be recorded. Because many well purging techniques can allow aeration of collected groundwater samples, it is important to minimize the potential for aeration. Also, because of the difficulty in obtaining accurate dissolved oxygen measurements, especially when the concentration falls below about 1 milligram per liter, these measurements should be used in a qualitative manner. One use of dissolved oxygen measurements is to determine stabilization

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during well purging. Stabilization of dissolved oxygen concentrations, in conjunction with pH, temperature, and conductivity, can be useful during well purging to determine when the well has been purged sufficiently to give representative samples.

Nitrate

After dissolved oxygen has been depleted in the microbiological treatment zone, nitrate is used as an electron acceptor for anaerobic biodegradation of organic carbon via denitrification. During denitrification, nitrate concentrations measured in groundwater decrease. Thus, nitrate concentrations below background in areas with dissolved contamination provide evidence for denitrification. Nitrate is an electron acceptor that competes with dehalorespiration. The absence of nitrate is a prerequisite for iron- and sulfate-reduction so it is important that this compound is absent in groundwater for biological and abiotic reactions to proceed.

Fe(II)

When Fe(III) is used as an electron acceptor during anaerobic biodegradation of organic carbon, it is reduced to Fe(II), which is somewhat soluble in water. Fe(II) concentrations are used as an indication that anaerobic degradation of organic carbon has occurred via Fe(III) reduction. The presence of Fe(II) (and sulfide) is required in order for many of the abiotic degradation reactions to occur. In addition, it has been shown by Bradley and Chapelle (1996; 1997) that vinyl chloride and DCE can be biologically oxidized under iron-reducing conditions. Fe(III) is an electron acceptor that competes with dehalorespiration.

Sulfate and Sulfide

Sulfate is used as an electron acceptor for anaerobic biodegradation during sulfate reduction wherein sulfate (SO_4^{2-}) is reduced to sulfide (HS^- or H_2S). During this process, sulfate concentrations measured in groundwater decrease and sulfide is produced. The sulfide produced during sulfate reduction is very reactive and in most cases is quickly complexed with Fe(II). From the standpoint of chlorinated solvent degradation, sulfate reduction is important for two reasons; 1) reductive dechlorination caused by biological processes does not become efficient until the dominant terminal-electron accepting process (TEAP) is sulfate reduction or methanogenesis, and 2) sulfate reduction is important for abiotic mechanisms of reductive dechlorination because it results in the production of sulfide. High sulfate concentrations will likely have the following two ramifications:

1) They will reduce the efficiency of biological reductive dechlorination because sulfate is a competing electron acceptor, and

2) They will increase the efficiency of abiotic reductive dechlorination, especially if appreciable amounts of Fe(II) are present.

Methane

As implied by the name, methanogenesis results in the production of methane during the biodegradation of organic carbon. The presence of methane in groundwater is indicative of strongly reducing conditions and biologically mediated reductive dechlorination is typically very efficient under these conditions. Analysis of methane concentrations in groundwater should be

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conducted by a qualified laboratory. It is important that the detection limit for methane be on the order of 1 μg/L, especially when evaluating the natural attenuation of chlorinated solvents.

The presence of methane generally is indicative of a Type I/Type II Environment (as described in Wiedemeier *et al.*, 1999) where reductive dechlorination to VC and then to ethene/ethane is likely. If no VC is present then abiotic reactions should be evaluated. Methane can also be transported by advective groundwater flow. Because of this its presence in a groundwater does not ensure that the immediate environment is methanogenic; only that methanogenic conditions exist in the vicinity. Evaluating the presence of methane in concert with the other geochemical indicators (e.g., Fe[II] and SO_4^{2-}) is essential.

Ethene/Ethane

Ethene and ethane are the end products of both biological and abiotic reductive dechlorination. Because these compounds are extremely transitory their concentrations typically remain low with concentrations at sites with active reductive dechlorination on the order of hundreds of micrograms per liter.

Alkalinity

Biologically active portions of a dissolved contaminant plume typically can be identified by an increase in alkalinity. This increase in alkalinity is brought about by the production of carbon dioxide during the biodegradation of organic carbon. Alkalinity results from the presence of hydroxides, carbonates, and bicarbonates of cations such as calcium, magnesium, sodium, and potassium. These species result from the dissolution of rock (especially carbonate rocks), the

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transfer of carbon dioxide from the atmosphere, and respiration of microorganisms. Alkalinity is important in the maintenance of groundwater pH because it buffers the groundwater system against acids generated during both aerobic and anaerobic biodegradation. In general, areas with reduced organic carbon exhibit a total alkalinity that is higher than that seen in those areas with low organic carbon concentrations. This is expected because the microbially-mediated reactions causing biodegradation of organic carbon cause an increase in the total alkalinity in the system. Changes in alkalinity are most pronounced during aerobic respiration, denitrification, Fe(III) reduction, and sulfate reduction, and less pronounced during methanogenesis (Morel and Hering, 1993).

Chloride

During biodegradation of chlorinated hydrocarbons dissolved in groundwater, chloride is released into the groundwater, resulting in the accumulation of biogenic chloride. This results in chloride concentrations in groundwater in the contaminant plume that are elevated relative to background concentrations. In aquifers with low background concentrations of chloride, the concentration of this material in the solute plume can be seen to increase as chlorinated solvents are degraded.

Elemental chlorine is the most abundant of the halogens. Although chlorine can occur in oxidation states ranging from Cl^- to Cl^{+7}, the chloride form (Cl^-) is the only form of major significance in natural waters (Hem, 1985). Chloride forms ion pairs or complex ions with some of the cations present in natural waters, but these complexes are not strong enough to be of significance in the chemistry of fresh water (Hem, 1985). The chemical behavior of chloride is

neutral. Chloride ions generally do not enter into oxidation-reduction reactions, form no important soluble complexes with other ions (unless the chloride concentration is extremely high), do not form salts of low solubility, are not significantly adsorbed on mineral surfaces, and play few vital biochemical roles (Hem, 1985). Thus, physical processes control the migration of chloride ions in the subsurface. Kaufman and Orlob (1956) conducted tracer experiments in groundwater, and found that chloride moved through most of the soils tested more conservatively (i.e., with less retardation and loss) than any of the other tracers tested. Because of the neutral chemical behavior of chloride, it can be used as a conservative tracer to estimate biodegradation rates.

References

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Wiedemeier, T.H., and Haas, P.E. 2002, Designing Monitoring Programs to Evaluate the Performance of Natural Attenuation: Ground Water Monitoring and Remediation, Summer 2002.

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SENSITIVE RECORD

PORTIONS OF THIS RECORD ARE CONSIDERED SENSITIVE
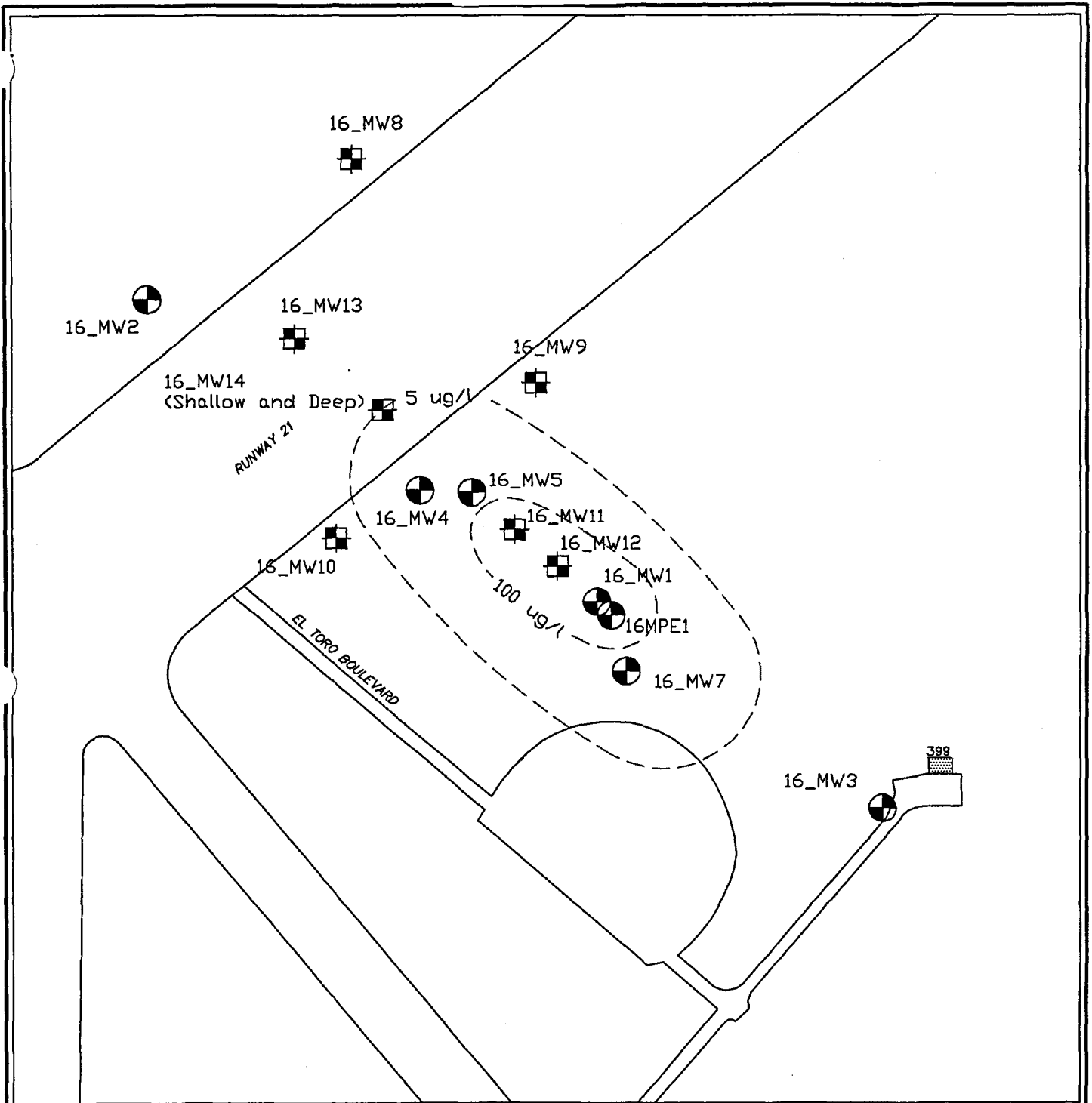AND ARE NOT AVAILABLE FOR PUBLIC VIEWING

FIGURE 1 – EXISTING AND PROPOSED
MONITORING WELLS FOR EVALUATING MONITORING
NATURAL ATTRENUATION

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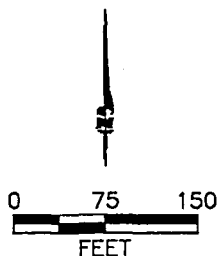TELEPHONE: (619) 556-1280
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Figure 1

Existing and Proposed Monitoring Wells
For Evaluating Monitored Natural Attrenuation

El Toro MCAS - Site 16

Date: 8/20/03
Client: U.S. Navy
Project Number:
Revision Number: 1

LEGEND

Existing Wells to be Sampled
for MNA Parameters

Proposed New Wells to be
Sampled for MNA Parameters

TCE Isopleth (ug/L)

Modified from Bechtel Environmental Inc., 2002

0   75   150
FEET
SCALE: 1 inch = 150 feet

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Table 1
New and Proposed Monitoring Wells to be Sampled
for the Evaluation of Monitored Natural Attenuation

Monitoring Well	Status
16_MW1	Active Well
16_MW2	Active Well
16_MW3	Active Well
16_MW4	Active Well
16_MW5	Active Well
16_MW7	Active Well
16_MPE1	Active Well
16_MW8	Proposed Monitoring Well
16_MW9	Proposed Monitoring Well
16_MW10	Proposed Monitoring Well
16_MW11	Proposed Monitoring Well
16_MW12	Proposed Monitoring Well
16_MW13	Proposed Monitoring Well
16_MW14S	Proposed Monitoring Well
16_MW14D	Proposed Monitoring Well

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Table 2
Aquifer Data Required to Evaluate Monitored Natural Attenuation

Analysis	Method	Data Use	Comments
Total Organic Carbon	SW9060 modified for soil samples	Sorption/solute retardation calculations	Procedure must be accurate over the range of 0.1–5 percent TOC
Bulk Density	Geotechnical Laboratory Procedure	Sorption/solute retardation calculations	May be estimated from literature values
Hydraulic Gradient	Determine from site potentiometric surface maps	Estimation of seepage velocity. Required for groundwater flow and solute transport models	At least three measurement points required
Hydraulic Conductivity	Slug tests or pumping tests	Estimation of seepage velocity. Required for groundwater flow and solute transport models	Critical parameter with the potential for the most measurement error. Sensitivity analyses on this parameter may be useful when estimating seepage velocity.
Total and Effective Porosity	Tracer tests or estimates from literature values	Estimation of seepage velocity. Required for groundwater flow and solute transport models	Literature values typically are used
Field observation of reduced iron minerals	Visual observation	Estimation of the potential for abiotic degradation through reaction with reduced iron minerals	Oxidized iron minerals are typically impart some shade of rust color to the soil ranging from rusty brown, to yellow or orange, to red or maroon. Reduced iron minerals typically cause the soil to be gray to black in color.
Laboratory Analysis for Reduced Iron Minerals	Mineralogical assay	Useful for deducing if anaerobic reductive dechlorination is or could be an important process.	Estimation of the potential for abiotic degradation through reaction with reduced iron minerals

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Table 3
Groundwater Data Required to Evaluate Monitored Natural Attenuation

Analysis	Method/Reference	Comments	Data Use	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Chemicals of Concern	SW8260B, 8270C, and 8015-M	Handbook method	Used to determine presence of parent and daughter compounds and rates of attenuation	Contact Laboratory	Fixed-base laboratory
Dissolved Oxygen	E360.1- Dissolved oxygen membrane electrode.	Avoid exposure to atmospheric oxygen.	Concentrations less than 1 mg/L generally indicate an anaerobic pathway	Measure dissolved oxygen onsite using a flow-through cell	Field
Nitrate	IC method E300	Method E300 is a Handbook method.	Substrate for microbial respiration if oxygen is depleted. Absence is required for Fe(III) reduction to occur	Collect 1x1 Liter poly container and cool to = 4 °C	Fixed-base laboratory
Iron (II) (Fe^{2+})	Colorimetric Hach Method	Filter with 0.45 micron inline filter.	Indicates an anaerobic degradation process due to depletion of oxygen, nitrate, and manganese. Required for abiotic reductive dechlorination.	Collect 100 mL of water in a headspace-free container to eliminate introduction of oxygen and analyze as soon as possible	Field
Sulfate (SO$_4^{2-}$)	IC Method E300	Method E300 is a Handbook method	Substrate for anaerobic microbial respiration	Collect 1x1 Liter poly container and cool to = 4 °C	Fixed-base laboratory
Sulfide	E376.1	Handbook method	Required for abiotic reductive dechlorination		Fixed-base laboratory
Methane, Ethane, and Ethene	RSK-175	Method published by researchers at the US EPA.	The presence of methane suggests biodegradation via methanogenesis. Ethane and ethene are daughter products of complete dechlorination.	Collect 6x40 mL VOA vials, preserve with HCL, and cool to cool to = 4 °C	Fixed-base laboratory
Bicarbonate and Carbonate Alkalinity	Hach digital titrate	Field filter with 0.45 micron inline filter.	General water quality parameter used to measure the buffering capacity of groundwater	Collect 100 mL of water in glass container. Analyze as soon as possible	Field
Chloride	IC method E300 *	Method SW9050 may also be used	Final product of chlorinated solvent reduction. Can be used as a tracer.	Collect 1x 1 Liter poly container and cool to = 4 °C	Fixed-base laboratory
Dissolved Organic Carbon	E415.1	Field filter with 0.45 micron inline filter. Minimize aeration and fill sample container completely.	Used to classify plume and to evaluate the potential for biologic and biologically predicated abiotic degradation.	Collect 1x250 mL glass amber container, preserve with H2SO4 and cool to = 4 °C	Fixed-base laboratory
PH	E150.1 - Field probe with direct reading meter.	Field	Fundamental measurement which is critical for interpretation of carbonate data. Used as a well stabilization criterion.	Measure in flow-through cell during well purging.	Field
Temperature	170.1 - Field probe with direct reading meter.	Field only	Fundamental measurement required in all thermodynamic calculations.	Measure in flow-through cell during well purging.	Field
Conductivity	E120.1/SW9050, direct reading meter	Protocols/Handbook methods	General water quality parameter that is proportional to the dissolved ions present in solution.	Measure in flow-through cell during well purging	Field

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